Interaction Between Ceria and Hydroxylamine

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Abstract

Ceria containing slurries are increasingly used in the chemical mechanical polishing of CVD silicon oxide films to obtain STI structures. Unlike silica or alumina, ceria has redox characteristics. Because of this characteristic, removal of ceria particles from planarized surfaces may be possible using chemical reagents that can participate in redox reactions. One such reagent is hydroxylamine, which is already being used in copper CMP. The objective of the work reported in this paper was to characterize the reaction between ceria and hydroxylamine, especially with respect to dissolution of ceria particles. A kinetic study of the dissolution of ceria in hydroxylamine solutions maintained at various pH values has been performed. The extent and kinetics of dissolution of ceria has been determined by ICPMS. Removal of ceria particles from oxide surfaces using hydroxylamine-based chemistries has been investigated.

Introduction

Chemical mechanical polishing of CVD silicon oxide films is a key step in forming [1] shallow trench isolation (STI) structures. Both silica [2] and ceria based [3] slurries have been used for this process. Silica based slurries often result in over polishing of certain features. Reports indicate that ceria slurries show promise in polishing STI structures without using the reverse mask process and stop on SiN layers [4]. Properly formulated ceria slurries appear to achieve STI pattern planarization with minimal oxide erosion [5].

Post CMP cleaning of the polished wafers to remove particles adhering to the wafers is very critical. The effectiveness of the cleaning process can be enhanced if the particles can be partly dissolved such that the adhesion between the particles and wafer can be reduced. Unlike silica or alumina, ceria has redox characteristics. Because of this characteristic, removal of ceria particles from planarized surfaces may be possible using chemical reagents that can participate in redox reactions. Under such conditions the parameters like solution redox potential (controlled by concentrations of redox agent), pH, and the presence of a chemical that can adsorb on the dislodged particles and prevent its redeposition can modulate the cleaning efficiency. One such redox reagent is hydroxylamine, which is already being used in copper CMP [6,7]. Hydroxylamine tends to function as an oxidizing agent at acidic pH values and as a reducing agent at alkaline pH values [8]. Dissolution of ceria particles in alkaline hydroxylamine chemistries, if it occurs, can be utilized to increase the effectiveness of cleaning.

The primary objective of the work reported in this paper was to characterize the reaction between ceria and hydroxylamine, especially with respect to dissolution of ceria particles. Based on the results from dissolution tests, a chemical formulation removing ceria particles from oxide surfaces has been developed and tested.

Materials and Methods

Potential-pH and solubility diagrams were constructed using the STABCAL computer software. The redox potentials of 3% ceria slurries in 0.01M potassium sulfate and in of 0.5M

hydroxylamine solutions were measured using an Orion platinum redox electrode. Dissolution experiments were carried out in a controlled environment laboratory scale reactor made of quartz. The amount of dissolved ceria in solution was determined by ICPMS. The zeta potential of ceria particles as a function of pH was measured using a DELSA 440 SX electrophoretic light scattering apparatus.

Post CMP cleaning tests were performed on 8-inch CVD oxide wafers (oxide thickness ~ 10kÅ). The wafers were polished on an IPEC 472 polisher using IC1000 – SUBA4 pad. Ceria based STI 100 RA3 slurry (mean particle size of 130 nm; pH of 4.9) marketed by EKC Technology was used in the polishing step. The polishing was done for 20 seconds at a down force of 2psi. The polished wafers were buffed with ultra pure DI water for 10 seconds at a down force of 1psi. In both the polishing and buffing steps, the platen and wafer were rotated at 100 and 107 rpm respectively. The wafers were then rinsed in DI water for 30 seconds. The rinsed wafers were cleaned in a SSEC megasonic cleaner (1.5MHz), for 10 cycles (100-300 sec) with the chemical solution flowing at 480ml/min. The cleaned wafers were spin dried and analyzed for defects using a KLA SP1 surface scanner.

Results and Discussion

Pourbaix diagrams were constructed at three different activities of cerium species (0.1, 0.0001 and 0.000001M) and are shown in figure 1. The solid cerium species, Ce, CeO_2, Ce_2O_3, CeH_2, $Ce(OH)_3$ and aqueous cerium species Ce^{2+}, Ce^{3+}, Ce^{4+}, $CeOH^{3+}$, $Ce(OH)_2^{2+}$, $Ce_2(OH)_3^{5+}$, $Ce_2(OH)_4^{4+}$, $Ce_3(OH)_5^{4+}$ and $Ce_6(OH)_{12}^{12+}$ were considered in drawing the diagram. It can be seen that the Ce^{3+}, $Ce(OH)_3$ and CeO_2 are the most stable species in the water stability region shown by the dotted lines (solid CeO_2 occupies the major portion of the water stability region). The Ce^{3+} species is stable in highly acidic regions (pH< 1) at all potential conditions, but as the pH increases CeO_2 becomes stable at higher potentials. The solid $Ce(OH)_3$ and CeO_2 dominate the neutral and alkaline regions. It can be seen that a decrease in the activity of the cerium species shifts the stability regions of Ce^{3+} to higher pH values.

Figure 2 shows the predicted (based on thermodynamic data) concentration of dissolved cerium as a function of pH at different solution potential values for a total (solid plus dissolved) cerium concentration of 0.1M in the system. At a potential of 0.0V (vs. SHE), the cerium may be predicted to be entirely in the form of dissolved species in the pH range of 0 to 6.5. In other words, if CeO_2, at a concentration of 0.1 M, were equilibrated with an aqueous solution maintained in the pH range of 0 to 6.5 and potential of 0.0mV, the oxide, based on thermodynamic considerations, would exhibit complete solubility. (However, the actual amount dissolved would depend on kinetic limitations.) As the potential increases, the pH range of complete solubility is gradually pushed towards the acidic side. At a solution potential of 1.0 volt, the solubility drops off steeply above a pH of 2.

The potential-pH diagram of the hydroxylamine water system is overlaid on that of the cerium – water system in figure 3. Hydroxylamine can be oxidized to HNO_2 (or NO_2^-, providing the electrons for reducing CeO_2 to Ce^{3+}. The redox behavior of hydroxylamine can enhance the dissolution of ceria. The measured redox potentials of 3% ceria slurries in the presence of 0.01M potassium sulfate as a supporting electrolyte and in the presence of 0.5M hydroxylamine are also plotted on the Pourbaix diagram of the Ce-water system in figure 3. It can be seen that the addition of hydroxylamine to the ceria suspension decreases the redox potential of the system. This decrease in redox potential is more evident in the alkaline regions. Thus the addition of hydroxylamine may increase the pH range of solubility of the ceria.
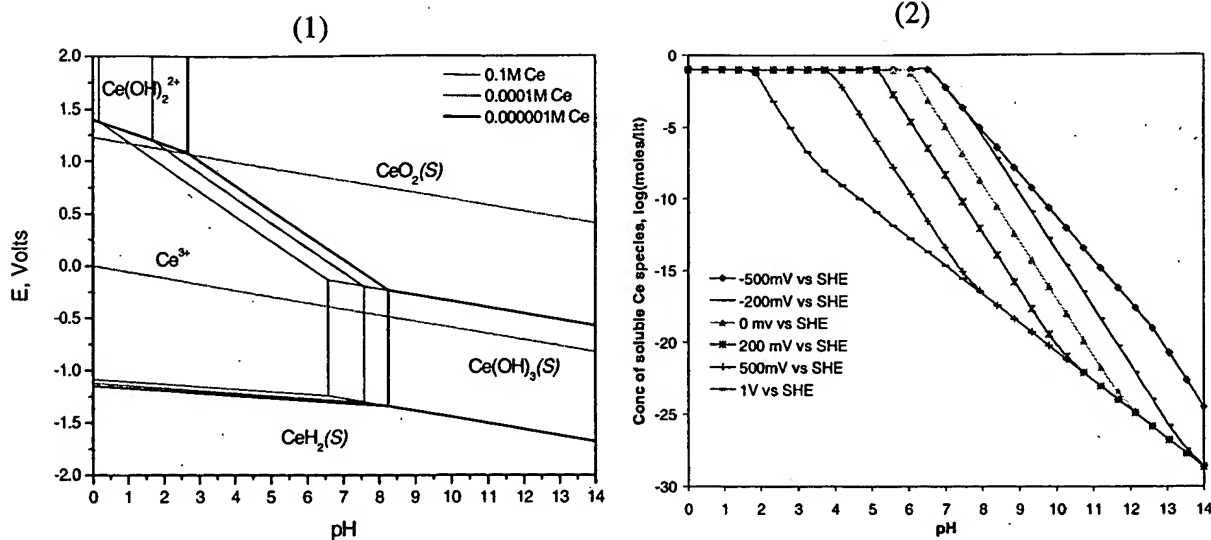
Figure 1: Potential – pH diagram of Cerium-Water system at different activities of soluble cerium species.

Figure 2: Concentration of dissolved cerium as a function of pH at various solution redox potentials.
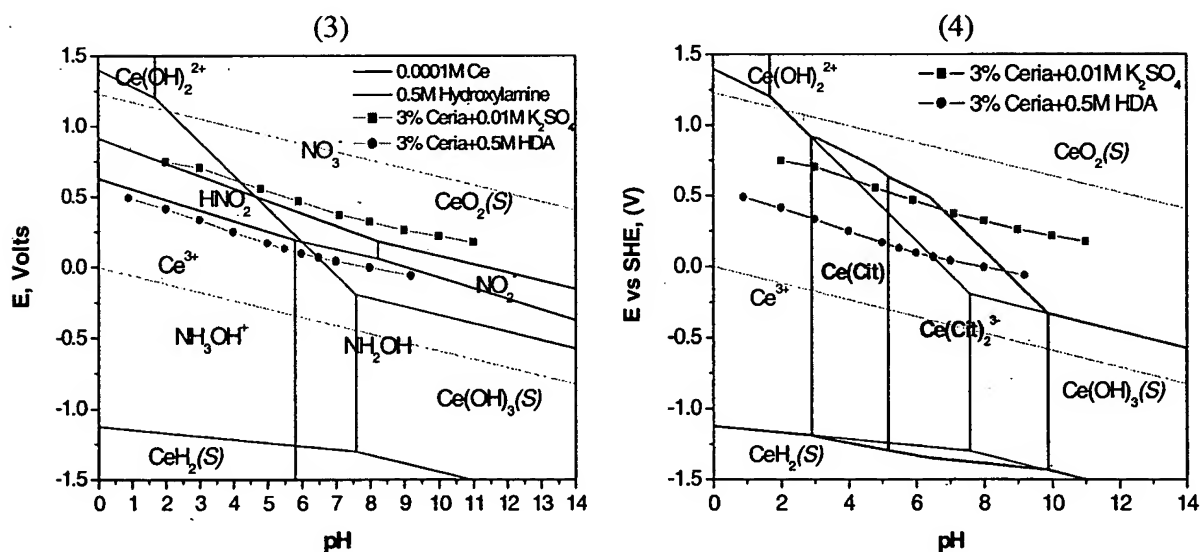

Figure 3: Potential-pH diagram of hydroxylamine water system overlaid on ceria-water system.

Figure 4: Potential-pH diagram of Ceria-citric acid-water system overlaid on ceria-water system

Addition of complexing agents to the cleaning solutions could enhance the dissolution of ceria particles and also prevent them from redepositing on the wafer surface. Citric acid forms a neutral and anionic complex with cerium [10] ($Ce(C_6H_5O_7)$ and $Ce(C_6H_5O_7)_2{}^{3-}$ with stability constants of $10^{7.4}$ and $10^{10.4}$). Figure 4 shows the potential-pH diagram of a cerium-citric acid-

water system overlaid on that for cerium-water system. It can be seen that Ce^{+3}–citrate complexes are stable in a wide range of pH values. Thus, it may be expected that reductive dissolution of CeO_2 in citric acid solutions is possible if a suitable reducing agent is used. From the values of redox potentials of hydroxylamine solutions at different pH values, it may be concluded that hydroxylamine-citrate solutions would be a suitable chemical formulation to dissolve CeO^2.

The dissolution kinetics of ceria in 0.5M hydroxylamine solutions is shown in figure 5 as a function of pH. It can be seen that the dissolution kinetics strongly depends on the pH of the system. At acidic conditions (pH<6), CeO_2 is reduced to soluble Ce^{3+}. In the neutral and alkaline conditions (pH>6), formation of Ce^{3+} is not favorable and hence a lower dissolution is observed. It is evident that the solubility of ceria at alkaline conditions cannot be enhanced just by the addition of a reducing agent (hydroxylamine).

In cases where citric acid was added to hydroxylamine solutions, enhanced solubility of ceria is observed as shown in figure 6a. The increase in solubility is due to the complexation of ceria by citric acid. The highest dissolution is obtained at 0.01M citric acid in both the pH conditions. From the potential-pH diagram of the cerium-citric acid system shown earlier, a similar amount of dissolution of ceria will be expected at pH 6 and 8 due to the presence of similar Ce-citrate complexes. However, interestingly the dissolution at pH 8 is greater than at pH 6.
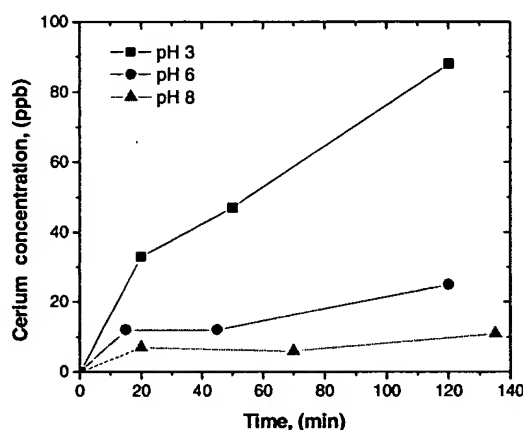

Figure 5: Dissolution kinetics of ceria (0.01 %) in 0.5 M hydroxylamine solutions at different pH values.

In the absence of hydroxylamine, the dissolution of ceria at pH 6 and 8 follows the same trend (figure 6b). Thus it can be concluded that hydroxylamine hinders the dissolution of ceria at pH 6. The peculiar behavior at pH 6 can be explained by the speciation in the hydroxylamine system. Hydroxylamine has a pKa of 5.8 and can exist in a protonated form (NH_3OH^+) below that pH. Therefore, in the vicinity of pH 6, both NH_2OH and NH_3OH^+ species are present. Under these conditions hydroxylamine is known to undergo disproportionation reactions (auto oxidation and reduction) to produce NH_4^+ (reduced form) and N_2, N_2O, and NO_2^- (oxidized forms). The disproportionation of NH_2OH and NH_3OH^+ could enable the formation of $Ce(OH)_3$

that has a poor solubility, thereby reducing the dissolution of ceria. The proposed redox reactions at pH 6 are given below,

Oxidation:
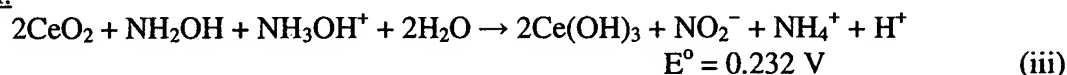$$NH_2OH + NH_3OH^+ \rightarrow NO_2^- + NH_4^+ + 3H^+ + 2e^- \quad E^o_{oxdn} = 0.162 \text{ V} \quad \text{(i)}$$

Reduction:
$$CeO_2 + e^- + H^+ + H_2O \rightarrow Ce(OH)_3 \quad E^o_{redn} = 0.070 \text{ V} \quad \text{(ii)}$$

Overall:
$$2CeO_2 + NH_2OH + NH_3OH^+ + 2H_2O \rightarrow 2Ce(OH)_3 + NO_2^- + NH_4^+ + H^+$$
$$E^o = 0.232 \text{ V} \quad \text{(iii)}$$

Equation (iii) clearly shows that solid $Ce(OH)_3$ species can be formed at pH 6 in the presence of hydroxylamine. Though the potential-pH diagram predicts the formation of soluble cerium-citrate complex, it must be noted that the interaction of hydroxylamine was not considered in the construction of the diagram. Therefore, it is likely that ceria forms a metastable hydroxide instead of a citrate complex at pH 6 in the presence of both hydroxylamine and citric acid. Hydroxylamine does not affect the dissolution at pH 8 due to the absence (very low) of protonated hydroxylamine.
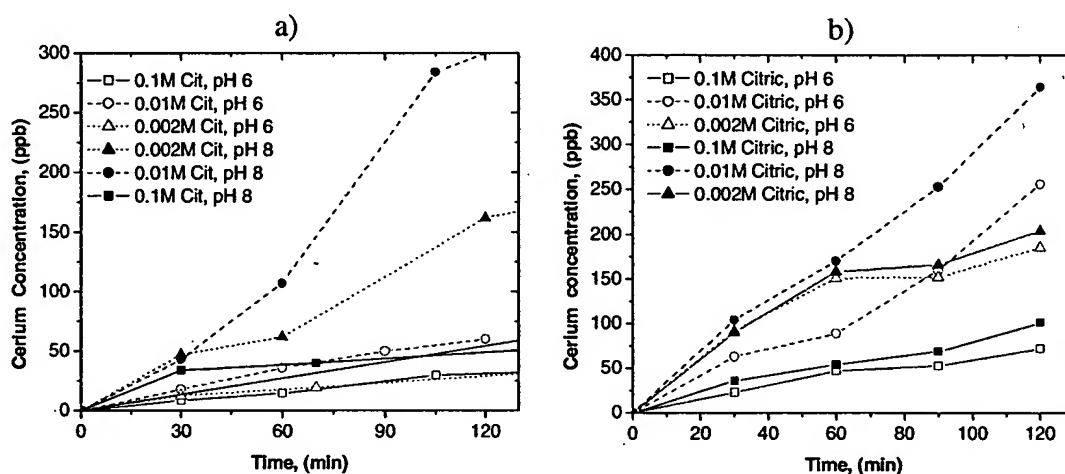

Figure 6: Dissolution of ceria (0.01%) in, a) 0.5M hydroxylamine solutions containing various levels of citric acid, b) citric acid solutions (no hydroxylamine)

The effectiveness of hydroxylamine chemistries (with citric acid) in cleaning (8 inch) polished wafers is shown in figure 7a. Cleaning tests with pure DI water (in the presence of megasonic scrubbing) is not effective as the LPD counts (light point defect count) are as high as 1200. Cleaning with hydroxylamine chemistries maintained at pH 8 brings down the LPD counts. The solution containing 0.1M hydroxylamine and1000 ppm citric acid provides the best cleaning in 100 seconds. Figure 8b shows the effect of cleaning time. It can be seen that the number of defects decrease with increase in cleaning time. The increase in cleaning time in the 0.1M hydroxylamine-citric acid chemistry brings down the LPD counts from 636 to 422. The results from the cleaning tests clearly show the ability of hydroxylamine-citric acid chemistries to

remove ceria particles from the polished oxide wafers. Further testing is needed to optimize the chemical composition and cleaning conditions.
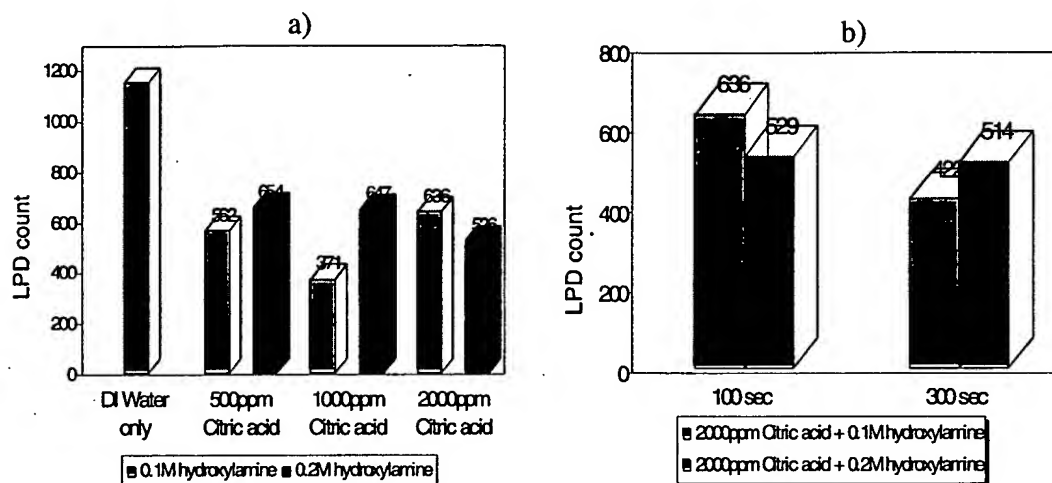
a)

b)

Figure 7: Cleaning of oxide wafers, a) in various chemistries (100sec), b) at different cleaning time.

Conclusions

Hydroxylamine by itself does not increase the solubility of ceria particles but is effective when used in conjunction with a complexing agent like citric acid. At a pH value close to its pKa, hydroxylamine hinders the complexation between cerium ions and citric acid by the formation of a metastable cerium hydroxide and thereby reducing the dissolution of ceria. Preliminary cleaning tests show that hydroxylamine-citric acid based chemistries can be used in removing ceria particles from planarized oxide wafers.

References:

[1] Zhao, E., Xu, C. S., Semiconductor International p. 145, June (2001).

[2] Lee, S. et. al; Proceedings of the CMP-MIC Conference. p. 163, (2000).

[3] Bonner, B. et. al; Proceedings of the CMP-MIC Conference. p. 572, (2001).

[4] Maria A. Lester, Semiconductor International, May (2002).

[5] Leduc, P. et. al; "CMP: Aiming for Perfect Planarization," Proceedings of the CMP-MIC Conference. p. 239, (2002).

[6] R.J. Small, L. McGhee, D. Maloney and M.L. Patterson, "Chemical mechanical polishing chemicals and process", WO Patent 98/04646, (1998).

[7] M.L. Peterson, R.J. Small, T. Truong and J. Lee, Semiconductor Fabtech, 11th edition, (2000).

[8] M. Van der Puy and J.H. Dimmit, *Hydroxylamine: Redox Properties of Hydroxylamines, Part 1. Inorganic Reactions*. Technical Bulletins, AlliedSignal Inc., (1985).

[9] S. Tamilmani, W. Huang, S. Raghavan and R. Small, Journal of The Electrochemical Society, 149 (12), G638-G642 (2002).

[10] A. E. Martell and R. M. Smith, *Critical stability constants*, Plenum, New York (1974).